Supporting Information

Toward a lithium-'air' battery:

The effect of CO_2 on the chemistry of a lithium-oxygen cell

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[Reference energy calculation of electron]

Quantum mechanical energy of electron is basically "0" value. However, considering the source of electron in Li-air battery system, some amount of energy is always required to generate electron from counter electrode. To calculate reasonable energy changes of reaction which is including electron, we have to take account ofenergy cost to dissolve a Li^+ into the electrolyte from Li solid. Calculation detail is as follows.

$$\begin{array}{ccccc} Li(crystal) & \xrightarrow{\Delta E_{1,cohesive}} & Li(g) & \xrightarrow{\Delta E_{2,ionization}} & Li^+(g) + e^- \\ & & \downarrow \Delta E_{3,solvation} & & \downarrow \Delta E_{4,solvation} \\ & & Li(solv.) & \xrightarrow{\Delta E_5} & Li^+(solv.) + e^- \end{array}$$

*Required energy to generate electron

$$\Delta E_{electron} = \Delta E_1 + \Delta E_3 + \Delta E_5$$

$$= \Delta E_1 + \Delta E_3 + (\Delta E_2 - \Delta E_3 + \Delta E_4)$$

$$= \Delta E_1 + \Delta E_2 + \Delta E_4$$

(kcal/mol)	ΔE1	ΔE2	ΔE3	ΔE4	ΔE5	**$\Delta E_{electron}$**
EC	39.0[1]	129.6	0.0	-135.7	-6.1	**32.9**
DMSO				-134.4	-4.8	**34.2**
DME				-118.1	11.5	**50.5**

(1) Silverman, R. A. et al.*Phys. Rev.***1950**, *80*, 912

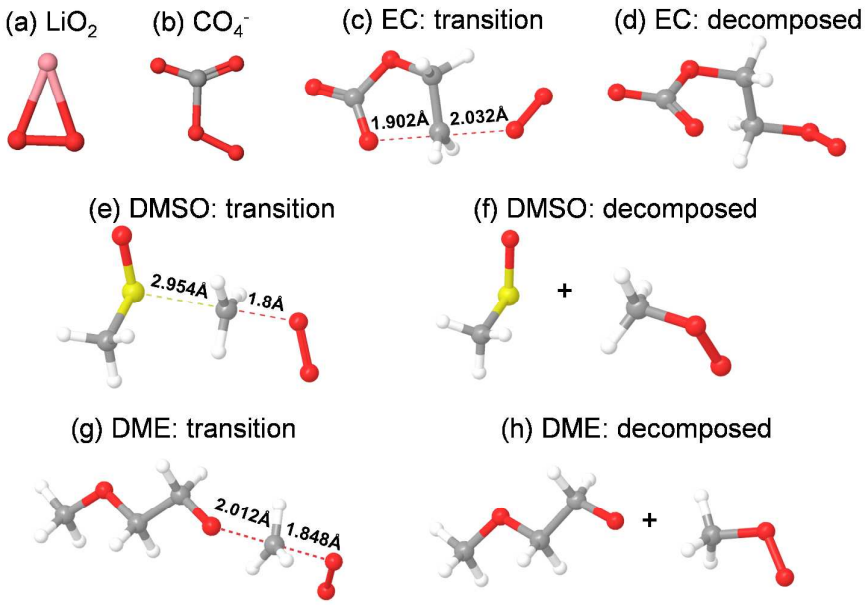

Figure S1. Structures of chemical species which are derived by initial reaction step with O_2^-; (a) $O_{2-} + Li^+ \rightarrow LiO_2$, (b) $O_2^- + CO_2 \rightarrow CO_4^-$, transition and decomposed state of EC (c and d), DMSO (e and f) and DME (g and h). (Atomic species: red-O, pink-Li, grey-C, white-H, yellow-S)

In case of EC, above decomposed structure (d) is not final decomposition state but intermediate state which is going to be decomposed further to CO_2 and lithium carbonate complexes.[2] Decomposition states of DMSO and DME are referred from previous research.[3]

(2) Freunberger, S. A. et al. *J. Am. Chem. Soc.***2011**, 133, 8040

(3) Bryantsev, V. S. et al. *J. Phys. Chem. A.* **2011**, 115, 12399

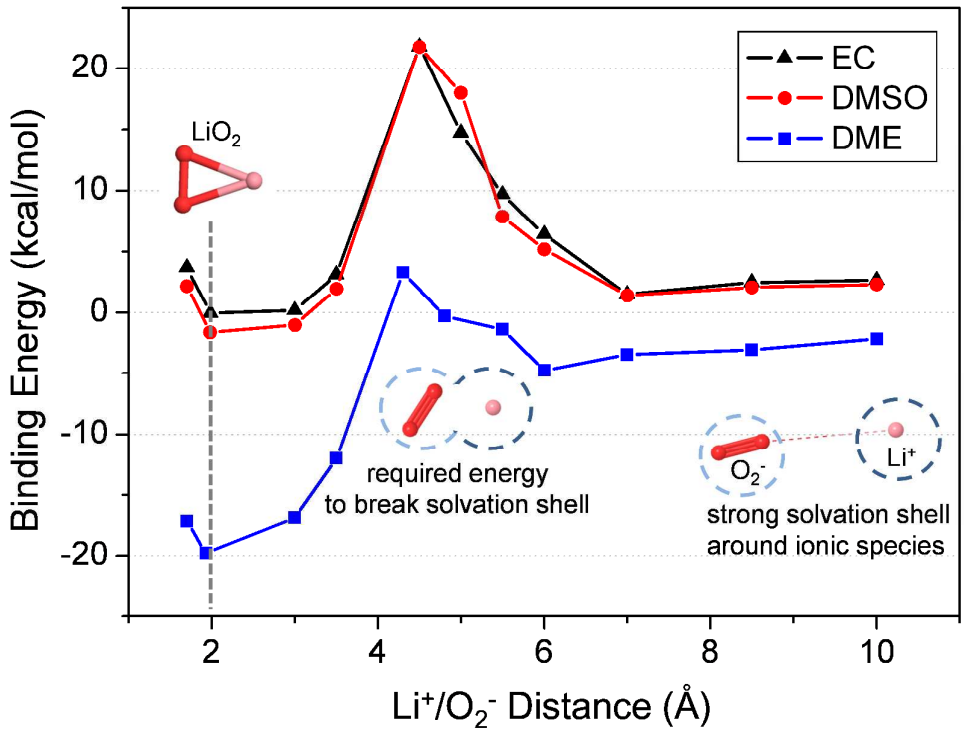

Figure S2. Binding energy trend of relaxed coordinate scan between O_2^- and Li^+under Poisson-Boltzmann solvation model within EC (triangle, black), DMSO (circle, red) and DME (square, blue).

Because of the strong Coulombic interaction between ionic species, the binding energy trend of O_2^- with Li^+ in gas phase along with the distanceis substantial downhill process with no activation barrier.The activation barrier is determined by choosing highest energy from relaxed coordinate scan energies under implicit solvation model.Activation barrier can be referred as the factor solely that comes from solvation effect.

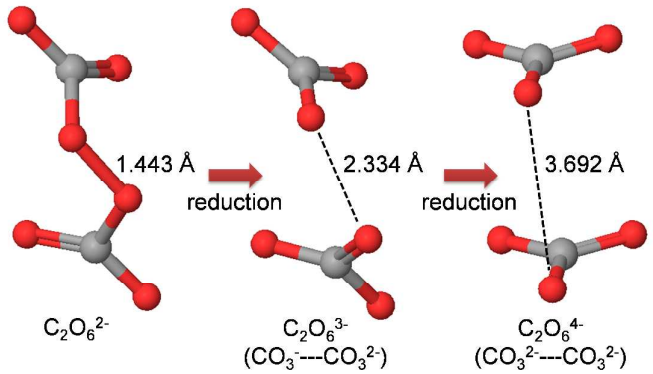

Figure S3. Detailed structures of dissociation process from $C_2O_6^{2-}$ to (CO_3^{2-}---CO_3^{2-}) by reduction under DMSO implicit solvation model

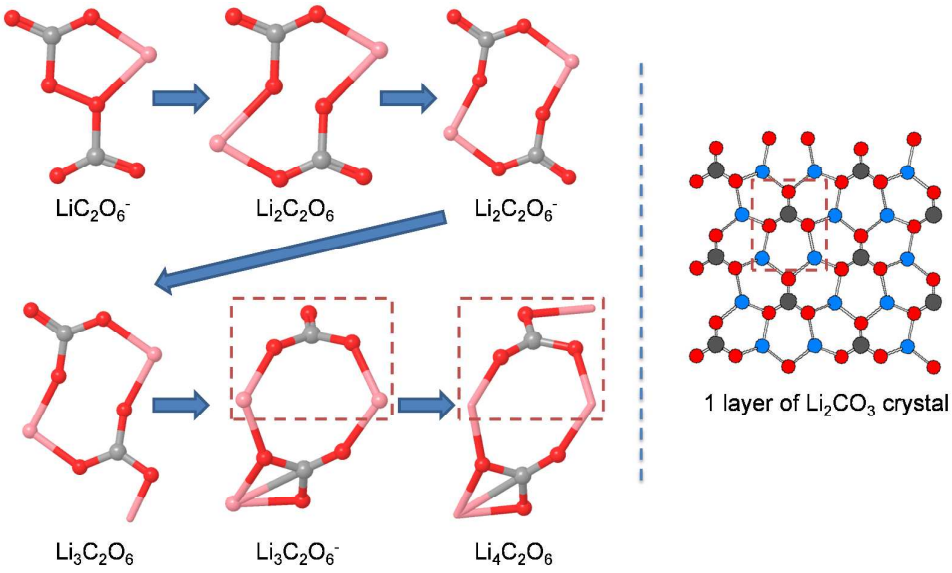

Figure S4. Reduction processes which include Li^+ effect from $C_2O_6^{2-}$ to $C_2O_6^{4-}$ under DMSO implicit solvation model. Result structure hassame topology with basic unit of actual Li_2CO_3 crystal.

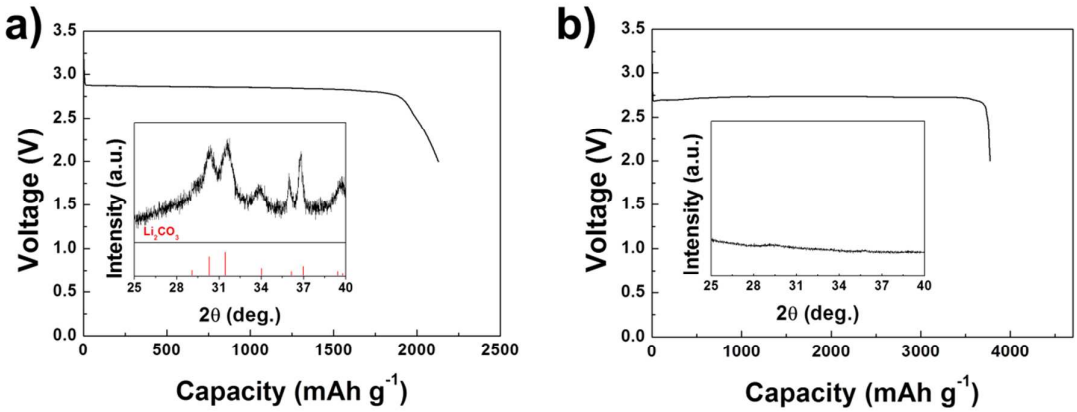

Figure S5. Electrochemical properties and XRD results of Li-O_2/CO_2 cells with (a) DMSO electrolyte and (b) DME electrolyte at a 9:1 pressure ratio of O_2 and CO_2.

Since the actual air condition always has a relatively lower CO_2 concentration than O_2, we further investigate the effect of CO_2 incorporation in an oxygen richcondition,which is closer to the ambient air condition.While the total outer pressure of 770 Torr is constantly maintained, the partial pressure ratio of O_2 and CO_2 is controlled at9:1. Interestingly, the Li-O_2/CO_2 cell with DMSO electrolyte in Figure S5a shows very similarreaction profile with Figure 5c, which impliesthat the CO_2 incorporation could be activated even in a relatively low CO_2 concentration.The final discharge product of $Li_2CO_3$is also solely detected.In comparison, amorphous phase of discharge products were formed in DME electrolyte (Figure S5b), which is very similar case with the cell at 1:1 ratio of gases as in case ofFigure 7d. The discharge products areLi_2O_2 and Li_2CO_3 from the FT-IR results (data not shown here). The discharge capacity has increased compared to the cell of O_2:CO_2 =1:1 ratio indicating that the overall discharge capacity is proportional to the partial pressure of oxygen in DME unlike the cased of DMSO. This result is quite meaningful because it is revealed that CO_2can greatly affect on the cell performance, even in the CO_2 deficiency atmosphere and it also suggest that

we have to consider the effect of CO_2 incorporation in further designing of Li-air cells operated in an ambient air system.